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APPLICATION OF MICROWAVE SPECTROMETRY FOR THE DETERMINATION OF ETHYL AND ISOPROPYL ALCOHOL IMPURITIES IN GASOLINE

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ABSTRACT. A wide-band microwave spectrometer designed by
the authors for analytical purposes is described and a
quantitative method for determining ethyl and isopropyl
alcohol impurities in gasoline is developed. The spectro-
meter described herein incorporates UHF tubes with crossed
fields as the emission source and permits measurement of
relative intensities in the 7,000 MHz band and higher. This
apparatus can be used for the quantitative and qualitative
analysis of multicomponent organic mixtures and has advan-
tages over methods such as IR-spectroscopy and chromato-
graphy. The analytical results are summarized in tables for
ethyl and isopropyl alcohol in gasoline.

Microwave spectroscopy has a high resolution capability and is much more   /1532[1]
effective than infrared spectroscopy. However, microwave spectroscopy has not
found general application in analytical chemistry. The principal reason for
this is the fact that it is impossible to measure the relative intensities of
spectral bands in a wide frequency range on the existing microwave spectro-
scopes. The authors of this work have designed and constructed a wide band
microwave spectrometer which makes it possible to measure relative intensities
in the 7,000-MHz range and higher. This is accomplished by using UHF tubes with
crossed fields(traveling-wave tubes, backward-wave tubes, etc.) as the source of
emission. This apparatus permits the qualitative and quantitative analysis of
multicomponent mixtures.

This article treats the quantitative analysis of a mixture of certain
organic compounds.

Apparatus. As the source of emission in our microwave spectrometer, we
used a tube with crossed fields and constant scanning without mechanical
retuning in a wide frequency range (7,000 MHz). We used a II-shaped wave guide
with a coaxial rectifier as the rectifier stage. This eliminated the need to
use frequency-dependent fine-tuning elements in the waveguide channel of the
apparatus. For the purpose of stabilizing the UHF-field in the region of the
rectifier, we used negative feedback for the direct component of the rectifier
current with a relative accuracy of $\pm 2\%$. The absorption cell, an ordinary

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[1] Numbers in the margin indicate pagination in the foreign text.

cell with an internal electrode, was placed in a thermostat. The Stark modulation frequency was 75 KHz. The absorption bands were recorded by an EPP-09 electron potentiometer connected to the output of the synchronous rectifier. The operating pressure in the cell was $1 \cdot 10^{-1}$ mm Hg.

Procedure for quantitative analysis. An internal standard is made for all samples and references. The spectra of the references are preliminarily photographed for the construction of a calculated graph. The partial pressure of the internal standard in the absorption cell is maintained constant throughout the absorption band. For the purpose of eliminating variations in the concentrations of the components in the liquid and gas phases, the sample was injected from an inlet space in which the liquid sample was completely vaporized. The effect of absorption on the walls of the cell was eliminated by maintaining a constant flow.

The measurement error consisted of the error related to the maintaining of the UHF-field voltage in the rectifier region and the error of the recording instrument. For the measurements of four absorption bands this error amounted to ±10%.

Theory of quantitative analysis. According to Esbit and Vil'son [1] the alternating component of the rectifier current is

$$i = -\alpha l_{ef} \pi^{-1} \left(\sum_{n=1}^{\infty} n C_c E^n \right) \sin \omega t, \tag{1}$$

where l_{eff} is the effective length of the cell, α is the absorption coefficient /1533 of the gas, C_c is the conversion coefficient of the rectifier, E is the voltage of the electrical field in the rectifier region, and ω is the frequency of modulation.

The relative intensity of the two bands of the various components of the mixture is

$$R = \frac{i_1}{i_2} = \frac{\alpha_1}{\alpha_2} \cdot \frac{l_{ef1}}{l_{ef2}} \cdot \frac{\sum\limits_{n=1}^{\infty} n C_c E_1^n}{\sum\limits_{n=1}^{\infty} n C_c E_2^n} \cdot \tag{2}$$

In using the method of quantitative analysis which incorporates the use of an internal standard in all reference and analyzed samples and the selection of one analytic band for each component of the mixture, we may use the equality

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$$\frac{R}{R_{re}} = \frac{\alpha_1}{\alpha_{st}} \left(\frac{\alpha_{st}}{\alpha_1}\right)_{re} \tag{3}$$

under the condition

$$\frac{l_{efl}}{l_{ef.st}} = \left(\frac{l_{efl}}{l_{ef.st}}\right) \quad \text{and} \quad \frac{E_1}{E_{st}} = \left(\frac{E_1}{E_{st}}\right)_{re}. \tag{4}$$

Condition (4) may be satisfied if there are no variations in the high-frequency channel of the apparatus in its entire frequency range during the analysis. Condition (4) is satisfied and formula (3) is valid for the determination of relative intensities when performing analyses on the apparatus designed by the authors, which does not have fine-tuning elements. Let us consider the ratio α_1/α_{st}. According to the theory of microwave spectroscopy [2], the absorption coefficient of a gas is

$$\alpha = \frac{8\pi n}{3ckT} (J|\overline{P}|J')^2 \frac{v^2}{\Delta v}, \tag{5}$$

where n is the number of molecules, c is the velocity of light, k is the Boltzmann constant, $(J|\overline{P}|J')$ is the matrix element of the dipole moment, v is the frequency of the absorption band, and Δv is a half-width of the band.

The values of $(J|\overline{P}|J')$ and v are determined by the properties of the molecule and by quantum transition, and are independent of the concentration of the substance in the mixture. The value of T must be maintained constant during the analyses. Thus formula (5) may be written as

$$\alpha = A \frac{n}{\Delta v}. \tag{6}$$

According to theory, a half-width Δv of a band depends on the partial pressures of the components in the mixture and on the parameters of the collisions of the molecules, i.e.,

$$\Delta v_1 = n_1\beta_{11} + n_2\beta_{12} + \ldots + n_m\beta_{1m}, \tag{7}$$

where n_1 and n_2 are the numbers of the molecules of components $1,2,\ldots$, in the mixtures; β_{11} is the contribution to the width of the band by the collisions of the molecules of component 1 with each other; β_{12} is the contribution to the width of the band by the collisions of the molecules of component 1 with those of component 2.

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Considering that energy is not transmitted from one molecule to another during a collision, the values of β_{11}, β_{12}, etc. may be represented in the form $\beta_{11} = \beta_1 \cdot \beta_1$, $\beta_{12} = \beta_1 \cdot \beta_2$, ..., whereupon the values of β_1, β_2, ... must depend only on the parameters of the corresponding component of the mixture. Formula (6) for the analyzed substance and for the internal standard will then acquire the form

$$\alpha_1 = A_1 \frac{n_1}{\beta_1 (n_1\beta_1 + n_2\beta_2 + \ldots + n_m\beta_m)}$$

and

$$\alpha_{st} = A_{st} \frac{n_{st}}{\beta_{st}(n_1\beta_1 + n_2\beta_2 + \ldots + n_m\beta_m)}$$

and we have the relation

$$\frac{\alpha_1}{\alpha_{st}} = \frac{A_1}{A_{st}} \cdot \frac{n_1}{n_{st}} \cdot \frac{\beta_{st}}{\beta_1} \tag{8}$$

By substituting formula (8) into expression (3) we obtain:

$$\frac{R}{R_{re}} = \frac{n_1}{n_{st}} \left(\frac{n_{st}}{n_1}\right)_{re} \tag{9}$$

Since $n = pC$, where p is the pressure of the sample in the absorption cell, and C is the concentration of a component of the mixture, and assuming that the concentration of the internal standard is constant in all samples ($C_{st} = C_{stre}$), we obtain

$$\frac{R}{R_{re}} = \frac{i_1}{i_{st}} \left(\frac{i_{st}}{i_1}\right)_{re} = \frac{C}{C_{re}}$$

The value of $(i_{st}/i_1)C_{re} = K$ is determined during the analysis of the reference sample and

$$C = K \frac{i_1}{i_{st}} \tag{10}$$

Thus the concentration of a given component of the mixture is proportional to the relative intensity of the bands of this component and of the internal standard, and is independent of the number of components in the mixture and of the pressure in the absorption cell under the following conditions: 1) there are no variations in the high-frequency channel of the microwave spectrometer throughout the entire frequency range; 2) the voltage of the UHF-field is constant in the rectifier region; 3) the temperature of the absorption cell is

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constant. These conditions are insured by the spectrometer under consideration.

Determination of the concentration of C_2H_5OH and $Iso-C_3H_7OH$ in Gasoline. For the purpose of testing the possibilities of conducting quantitative analysis of a multicomponent mixture on the microwave spectrometer, we determined the amount of ethyl and isopropyl alcohol in a complex organic mixture (in the 80-190-degree gasoline fraction). The analysis of this mixture by other analytic methods, including infrared spectroscopy and chromatography, is a difficult task.

Quantitative analysis was conducted in accordance with procedures outlined earlier with the application of two references and with the introduction of an internal standard in all samples. As the internal standard we used methyl alcohol, which was added to the samples and references in the quantity of 10% by volume (8 grams per milliliter).

For the analytic bands of ethyl and isopropyl alcohol, we chose the 26,510- and 26,820-MHz bands, respectively. The 26,847-MHz band of methyl alcohol was selected as the comparison band. The concentrations of ethyl and isopropyl alcohol were determined by a calibrated graph constructed on the basis of references with a known content of ethyl and isopropyl alcohol.

The results are listed in Table 1 (the average of two to five measurements). The reproducibility of the individual measurements is shown in Table 2 for several samples. It follows from these tables that the concentrations of ethyl and isopropyl alcohol in gasoline determined according to the relative intensities of the bands of the microwave spectrum are in good agreement with their actual concentrations.

Reproducibility is ±10%.

TABLE 1. DETERMINATION OF C_2H_5OH AND $ISO-C_3H_2OH$ CONCENTRATIONS IN GASOLINE

Sample No.	C_2H_5OH, %			$Iso-C_3H_7OH$, %		
	Used	Found	Difference	Used	Found	Difference
1	1.0	0.81	0.19	10.0	9.5	0.5
2	3.0	0.2	1.0	40.0	40.0	1.0
3	5.0	5.4	0.4	30.0	27.2	2.8
4	8.0	8.3	0.3	20.0	18.5	1.5
5	10.0	9.8	0.2	25.0	25.5	0.5
Reference 1	4.0			10.0		
Reference 2	20.0			40.0		

The mean relative calculation error was ~10%.

TABLE 2. REPRODUCIBILITY OF MEASUREMENT RESULTS

Sample No.	Measure-ment No.	Content, % by weight			
		C_2H_5OH		Iso-C_3H_7OH	
3	1	5,6	0.2	25,6	−1,6
	2	5,4	0	27,2	0
	3	5,2	+0,2	28,6	−1,4
	Average	5,4±0,2		27,2±1,0	
5	1	8,1	+1,7	25,8	+0,3
	2	10,1	−0,3	25,2	−0,3
	3	11,0	−1,2		
	Average	9,8±1,0		25,5±0,3	

Conclusions

We have described a wide-band microwave spectrometer designed by the authors for analytical purposes. We have developed a quantitative method for determining the ethyl and isopropyl impurities in gasoline.

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